

1 Statistical thermodynamics of free classical particles

Partition function of classical particles in $3d$ is defined as

$$\mathcal{Z}_{\text{class}} = \int d^3p \int d^3r \exp[-\beta E(\mathbf{p}, \mathbf{r})], \quad (1)$$

where $E(\mathbf{p}, \mathbf{r})$ is particle's energy. Note that this expression has the unit of (momentum \times distance)³, unlike the quantum partition function that is dimensionless. Define the density of states of a free classical particle in a box of volume V . By comparing it with the density of states for a quantum particle in a rigid box, find the missing factor in Eq. (1) that would make the classical partition function match the quantum one. This will define a quantum-mechanical “cell” in the phase space of a classical particle. Show that this quantum-mechanical aspect does not contribute into the internal energy and heat capacity of the classical particles.

Solution: The energy of the particle consists of the kinetic and potential energy,

$$E(\mathbf{p}, \mathbf{r}) = \frac{\mathbf{p}^2}{2m} + U(\mathbf{r}), \quad (2)$$

so that the classical partition function factorizes

$$\mathcal{Z}_{\text{class}} = \int d^3p e^{-\beta p^2/(2m)} \int d^3r e^{-\beta U(\mathbf{r})}. \quad (3)$$

For free particles there is no potential energy, and $\mathcal{Z}_{\text{class}}$ for particles in a rigid box of volume V becomes

$$\mathcal{Z}_{\text{class}} = V \int d^3p e^{-\beta p^2/(2m)}. \quad (4)$$

In the spherical coordinate system this becomes

$$\mathcal{Z}_{\text{class}} = 4\pi V \int p^2 dp e^{-\beta p^2/(2m)}. \quad (5)$$

Choosing the kinetic energy $\varepsilon = p^2/(2m)$ as the integration variable and using

$$p^2 = 2m\varepsilon, \quad dp = \frac{dp}{d\varepsilon} d\varepsilon = \frac{1}{2} \sqrt{\frac{2m}{\varepsilon}} d\varepsilon, \quad (6)$$

one can rewrite this in the form

$$\mathcal{Z}_{\text{class}} = \int_0^\infty d\varepsilon \rho_{\text{class}}(\varepsilon) e^{-\beta\varepsilon}, \quad \rho_{\text{class}}(\varepsilon) = 2\pi V (2m)^{3/2} \sqrt{\varepsilon}.$$

Quantum-mechanical partition function for this problem has the same form with

$$\rho(\varepsilon) = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon}. \quad (7)$$

The two densities of states are related as

$$\rho(\varepsilon) = \frac{\rho_{\text{class}}(\varepsilon)}{(2\pi\hbar)^3}$$

that defines the missing factor in the above definition of the classical partition function. Correcting $\mathcal{Z}_{\text{class}}$ as

$$\mathcal{Z}_{\text{class}} = \int \frac{d^3p d^3r}{(2\pi\hbar)^3} \exp[-\beta E(\mathbf{p}, \mathbf{r})], \quad (8)$$

one obtains the dimensionless quantity that coincides with the classical limit of the quantum partition function Z . This formula can be used in the presence of the potential energy as well.

The interpretation of the above is the following. The (x, p_x) projection of the phase space of the particle is discretized into cells $\Delta x \Delta p_x = 2\pi\hbar = h$, and the similar for other direction y and z . The cells have quantum origin and are related to the Heisenberg's uncertainty principle, stating that the product of uncertainties of measuring x and p_x of a quantum particle is of order h . The number of quantum cells in a limited region of x and p_x is limited and it defines the number of different states in this region. It is impossible to have more different states because there is no way to distinguish states that are too close both in x and in p_x by measurement.

Similarly quantum cells can be introduced in many-particle problems and in problems with rotational degrees of freedom. Quantum cells is an external element in classical statistical physics. Statistical averages of most physical quantities (except for the entropy and related functions) are insensitive to the quantization of the phase space of the system because the correction factor introduced above cancels.

2 Classical particles with gravity

Using the distribution function

$$f(\mathbf{p}, \mathbf{r}) = \frac{1}{\mathcal{Z}_{\text{class}}} \exp[-\beta E(\mathbf{p}, \mathbf{r})]$$

for classical particles with gravity, find the dependence of particle's concentration n and pressure P as the function of the height. Set the minimal height (the earth level) to zero. Calculate the heat capacity of this system and compare it with the one for free particles.

Solution: The energy of the particle has the form

$$E = \frac{p^2}{2m} + mgz.$$

The classical partition function of the particle factorizes:

$$\mathcal{Z}_{\text{class}} = \int d^3p \int d^3r \exp[-\beta E(\mathbf{p}, \mathbf{r})] = \mathcal{Z}_{\text{kinetic}} \mathcal{Z}_{\text{potential}},$$

where

$$\mathcal{Z}_{\text{kinetic}} = \int d^3p e^{-\beta p^2/(2m)}, \quad \mathcal{Z}_{\text{potential}} = \int d^3r e^{-\beta mgz}.$$

Here we do not use the phase-space quantization factor from the preceding problem because it will cancel out in the final results. The kinetic part of Z can be calculated as

$$\mathcal{Z}_{\text{kinetic}} = \left[\int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/(2m)} \right]^3 = (2\pi m k_B T)^{3/2}.$$

Assuming that the particles are contained to a vertical cylinder of the cross-section S (that is non-essential), for the potential partition function one obtains

$$\mathcal{Z}_{\text{potential}} = S \int_0^{\infty} dz e^{-\beta mgz} = \frac{S k_B T}{mg}.$$

Thus

$$\mathcal{Z}_{\text{class}} = \frac{S}{g} (2\pi)^{3/2} m^{1/2} (k_B T)^{5/2}.$$

Suppose there are N particles in the system. Then the number of particles in the element of the phase space is

$$dN = N f dp_x dp_y dp_z dx dy dz,$$

where f is the distribution function introduced above. The concentration of particles is defined as

$$n = \int d^3p \frac{dN}{dx dy dz} = N \int d^3p f.$$

Since f and $\mathcal{Z}_{\text{class}}$ factorize, the integrals over momentum cancel out and one obtains

$$n = \frac{N}{\mathcal{Z}_{\text{potential}}} e^{-\beta mgz}.$$

One can check that integrating this over the volume yields the identity $N = N$. Using the result for $\mathcal{Z}_{\text{potential}}$, one gets the final result

$$n = \frac{mgN}{S k_B T} e^{-\beta mgz}$$

that exponentially decreases with the height. For the pressure one does not have anything better than the ideal-gas formula

$$P = nk_B T = \frac{mgN}{S} e^{-\beta mgz}.$$

The average internal energy is given by

$$U = -N \frac{\partial \ln \mathcal{Z}_{\text{class}}}{\partial \beta} = -N \frac{\partial \ln \beta^{-5/2}}{\partial \beta} = \frac{5}{2} \frac{N}{\beta} = \frac{5}{2} N k_B T.$$

The heat capacity is

$$C = \frac{\partial U}{\partial T} = \frac{5}{2} N k_B.$$

This result might be unexpected. There is the heat capacity $(3/2)Nk_B$ from three translational degrees of freedom. Additionally, there is a potential energy for the motion in the vertical direction. Its contribution is Nk_B instead of the expected $(1/2)Nk_B$, as were the case for a vibrational degree of freedom. The reason for a different result is that the theorem of the equidistribution of the energy over degrees of freedom is valid in the cases when the energy is a quadratic function in momenta and deviations from the equilibrium positions (see the next problem). In our case, the potential energy is a linear rather than a quadratic function of z .

3 Classical harmonic oscillators in 3D

Consider classical particles with the potential energy

$$V(\mathbf{r}) = \frac{kr^2}{2}$$

in 3d. Calculate the partition function, internal energy and heat capacity.

Solution: We start, as usual, with calculating the classical partition function

$$\mathcal{Z}_{\text{class}} = \int d^3 p e^{-\beta p^2/(2m)} \int d^3 r e^{-\beta kr^2/2} = \mathcal{Z}_{\text{kinetic}} \mathcal{Z}_{\text{potential}}. \quad (9)$$

One obtains

$$\mathcal{Z}_{\text{kinetic}} = \left[\int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/(2m)} \right]^3 = (2\pi m k_B T)^{3/2}.$$

Similarly,

$$\mathcal{Z}_{\text{potential}} = \left[\int_{-\infty}^{\infty} dx e^{-\beta kx^2/2} \right]^3 = (2\pi k_B T/k)^{3/2}.$$

Thus

$$\mathcal{Z}_{\text{class}} \propto T^3 \propto \beta^{-3}.$$

The internal energy and heat capacity are given by

$$U = -N \frac{\partial \ln \mathcal{Z}_{\text{class}}}{\partial \beta} = \frac{3N}{\beta} = 3N k_B T$$

and

$$C = \frac{\partial U}{\partial T} = 3N k_B.$$

The factor 3 here is due to the three translational degrees of freedom of our system. Per each degree of freedom, there is $Nk_B/2$ due to the kinetic energy and the same amount due to the potential energy. This problem illustrates the equidistribution of energy over degrees of freedom in classical statistical physics.

4 Phonons in 1d and 2d

Calculate the internal energy and heat capacity of the system of harmonic phonons in one and two dimensions at low temperatures.

Solution: Instead of calculating the partition function, it is more convenient to use the direct formula for the internal energy

$$U = U_0 + \int_0^{\infty} d\omega \rho(\omega) \frac{\hbar\omega}{\exp(\beta\hbar\omega) - 1}, \quad (10)$$

where the upper limit of the integration has been set to infinity at low temperatures. In $2d$ the phonon density of states is

$$\rho(\omega) = \frac{S\omega}{2\pi v^2},$$

where S is the system's area. Discarding the zero-point energy U_0 , one obtains

$$U = \frac{S\hbar}{2\pi v^2} \int_0^\infty d\omega \frac{\omega^2}{\exp(\beta\hbar\omega) - 1} = \frac{S\hbar}{2\pi v^2} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^\infty dx \frac{x^2}{e^x - 1} = \frac{\zeta(3)S(k_B T)^3}{\pi v^2 \hbar^2}.$$

The heat capacity becomes

$$C = \frac{\partial U}{\partial T} = 3k_B \frac{\zeta(3)S(k_B T)^2}{\pi v^2 \hbar^2}.$$

5 Quantum correction to the heat capacity of the harmonic oscillator at high temperatures

Calculate the first quantum correction to the heat capacity of the harmonic oscillator at high temperatures.

Solution. The formula for the heat capacity of the ensemble of harmonic oscillators reads

$$C = Nk_B \left(\frac{\beta\hbar\omega_0}{\sinh[\beta\hbar\omega_0]} \right)^2. \quad (11)$$

At high temperatures (small β) one can expand this expression using the formula

$$\sinh x \cong x + \frac{x^3}{6}, \quad x \ll 1.$$

One writes

$$\left(\frac{x}{\sinh x} \right)^2 \cong \left(\frac{1}{1 + x^2/6} \right)^2 \cong (1 - x^2/6)^2 \cong 1 - x^2/3.$$

Thus, in the high-temperature range

$$C \cong Nk_B \left[1 - \frac{(\beta\hbar\omega_0)^2}{3} \right] = Nk_B \left[1 - \frac{1}{3} \left(\frac{\hbar\omega_0}{k_B T} \right)^2 \right].$$

The quantum correction contains \hbar and vanishes in the classical limit $\hbar \rightarrow 0$.

6 Magnetic susceptibility below T_C in the mean-field approximation

Calculate the zero-field magnetic susceptibility per spin below T_C in the mean-field approximation. Work out its form close to T_C

Solution. The spin polarization $\langle \hat{S}_z \rangle$ in the MFA satisfies the Curie-Weiss equation

$$\langle \hat{S}_z \rangle = b_S \left(\frac{g\mu_B B + Jz \langle \hat{S}_z \rangle}{k_B T} \right). \quad (12)$$

The magnetic susceptibility per spin is defined as

$$\chi = \frac{\partial \langle \mu_z \rangle}{\partial B} = g\mu_B \frac{\partial \langle \hat{S}_z \rangle}{\partial B}. \quad (13)$$

Using Eq. (12), one can write

$$\frac{\partial \langle \hat{S}_z \rangle}{\partial B} = b'_S \left(\frac{g\mu_B B + Jz \langle \hat{S}_z \rangle}{k_B T} \right) \left[\frac{g\mu_B}{k_B T} + \frac{Jz}{k_B T} \frac{\partial \langle \hat{S}_z \rangle}{\partial B} \right]. \quad (14)$$

This is an equation for the derivative that has the solution

$$\frac{\partial \langle \hat{S}_z \rangle}{\partial B} = \frac{g\mu_B}{k_B T} \frac{b'_S}{1 - b'_S \frac{Jz}{k_B T}}, \quad (15)$$

where the argument of b'_S is suppressed for brevity. It is convenient to express Jz via T_C using

$$T_C = \frac{S(S+1)}{3} \frac{Jz}{k_B}. \quad (16)$$

This yields

$$\frac{\partial \langle \hat{S}_z \rangle}{\partial B} = \frac{g\mu_B}{k_B T} \frac{b'_S}{1 - \frac{3b'_S}{S(S+1)} \frac{T_C}{T}}. \quad (17)$$

This is the solution of the problem at all temperatures. One has to solve the Curie-Weiss equation numerically to find $\langle \hat{S}_z \rangle$, and substitute it into the argument of b'_S .

The most important the zero-field susceptibility, $B = 0$. In this case, above T_C , one has $\langle \hat{S}_z \rangle = 0$, so that b'_S has zero argument, $b'_S(0) = S(S+1)/3$ and one obtains

$$\chi = \frac{\partial \langle \mu_z \rangle}{\partial B} = g\mu_B \frac{\partial \langle \hat{S}_z \rangle}{\partial B} = \frac{S(S+1)}{3} \frac{(g\mu_B)^2}{k_B T} \frac{1}{1 - \frac{T_C}{T}} = \frac{S(S+1)}{3} \frac{(g\mu_B)^2}{k_B (T - T_C)}. \quad (18)$$

Below T_C , there is a nonzero spin polarization, and one has to do some work to find $\langle \hat{S}_z \rangle$ just below T_C and substitute it into b'_S . The spin polarization for $S = 1/2$ has been found in the lecture for $S = 1/2$. Here we need to do it in general using the expansion

$$b_S(y) = \frac{1}{3}S(S+1)y - \frac{1}{90}S(S+1)(2S^2 + 2S + 1)y^3 + \dots \quad (19)$$

Then near T_C the Curie-Weiss equation with $B = 0$ becomes

$$\langle \hat{S}_z \rangle = \frac{1}{3}S(S+1) \frac{Jz \langle \hat{S}_z \rangle}{k_B T} - \frac{1}{90}S(S+1)(2S^2 + 2S + 1) \left(\frac{Jz \langle \hat{S}_z \rangle}{k_B T} \right)^3. \quad (20)$$

Canceling $\langle \hat{S}_z \rangle$ and expressing Jz via T_C , one simplifies this equation to

$$1 = \frac{T_C}{T} - \frac{3(2S^2 + 2S + 1)}{10[S(S+1)]^2} \left(\frac{T_C}{T} \right)^3 \langle \hat{S}_z \rangle^2 \quad (21)$$

that defines $\langle \hat{S}_z \rangle$ below T_C . It is convenient to write the solution as

$$\left(\frac{\langle \hat{S}_z \rangle}{S} \right)^2 = \left(\frac{T}{T_C} \right)^3 \frac{10(S+1)^2}{3(2S^2 + 2S + 1)} \left(\frac{T_C}{T} - 1 \right) = \left(\frac{T}{T_C} \right)^2 \frac{10(S+1)^2}{3(2S^2 + 2S + 1)} \left(1 - \frac{T}{T_C} \right), \quad (22)$$

to embrace the case $S \rightarrow \infty$. For the derivative $b'_S(y)$ we use the expansion

$$b'_S(y) = \frac{1}{3}S(S+1) - \frac{1}{30}S(S+1)(2S^2 + 2S + 1)y^2 + \dots \quad (23)$$

that follows from that for $b_S(y)$. In Eq. (17) one obtains

$$\frac{3b'_S}{S(S+1)} = 1 - \frac{2S^2 + 2S + 1}{10} \left(\frac{Jz \langle \hat{S}_z \rangle}{k_B T} \right)^2 = 1 - \frac{2S^2 + 2S + 1}{10} \left(\frac{3}{S(S+1)} \right)^2 \left(\frac{T_C}{T} \right)^2 \langle \hat{S}_z \rangle^2 \quad (24)$$

and, finally,

$$\frac{3b'_S}{S(S+1)} = 1 - \frac{9(2S^2 + 2S + 1)}{10(S+1)^2} \left(\frac{T_C}{T} \right)^2 \left(\frac{\langle \hat{S}_z \rangle}{S} \right)^2. \quad (25)$$

Substituting here the solution for the spin polarization, Eq. (22), one obtains

$$\frac{3b'_S}{S(S+1)} = 1 - \frac{9(2S^2 + 2S + 1)}{10(S+1)^2} \left(\frac{T_C}{T} \right)^2 \left(\frac{T}{T_C} \right)^2 \frac{10(S+1)^2}{3(2S^2 + 2S + 1)} \left(1 - \frac{T}{T_C} \right) = 1 - 3 \left(1 - \frac{T}{T_C} \right), \quad (26)$$

a big simplification! Now, substituting this into Eq. (17), one obtains

$$\chi = \frac{\partial \langle \mu_z \rangle}{\partial B} = g\mu_B \frac{\partial \langle \hat{S}_z \rangle}{\partial B} = \frac{S(S+1)(g\mu_B)^2}{3} \frac{1}{k_B T} \frac{1}{1 - \left[1 - 3\left(1 - \frac{T}{T_C}\right)\right] \frac{T_C}{T}} \quad (27)$$

and, simplifying the denominator,

$$\chi = \frac{S(S+1)(g\mu_B)^2}{3} \frac{1}{k_B T} \frac{1}{1 - \frac{T_C}{T} + 3\left(\frac{T_C}{T} - 1\right)} = \frac{S(S+1)(g\mu_B)^2}{3} \frac{1}{k_B T} \frac{1}{2\left(\frac{T_C}{T} - 1\right)}. \quad (28)$$

Finally, below T_C the zero-field susceptibility is

$$\chi = \frac{S(S+1)(g\mu_B)^2}{6} \frac{1}{k_B} \frac{1}{T_C - T}. \quad (29)$$

The coefficient here is two times smaller than that in the susceptibility above T_C . The general result near T_C can be written as

$$\chi = \frac{S(S+1)(g\mu_B)^2}{3} \frac{1}{k_B} \frac{1}{|T_C - T|} \begin{cases} 1, & T > T_C \\ 1/2, & T < T_C. \end{cases} \quad (30)$$

7 Two interacting Ising spins

Consider the model of two coupled spins with the Hamiltonian

$$\hat{H} = -g\mu_B B (S_{1,z} + S_{2,z}) - JS_{1,z}S_{2,z}.$$

Here B is the external magnetic field and J is the so-called exchange interaction, ferromagnetic for $J > 0$ and antiferromagnetic for $J < 0$. The model above in which only z components of the spins are coupled is called Ising model. The energy levels of this system are given by

$$\varepsilon_{m_1 m_2} = -g\mu_B B (m_1 + m_2) - Jm_1 m_2,$$

where the quantum numbers take the values $-S \leq m_1, m_2 \leq S$. Write down the expression for the partition function of the system. Can it be calculated analytically for a general S ? If not, perform the calculation for $S = 1/2$ only. Calculate the internal energy, heat capacity, magnetization induced by the magnetic field, and the magnetic susceptibility. Analyze ferro- and antiferromagnetic cases.

Solution: The partition function of the system is given by

$$\mathcal{Z} = \sum_{m_1, m_2 = -S}^S e^{-\beta \varepsilon_{m_1 m_2}}.$$

For a general spin S one can perform analytically only one summation. One can use the results for a single spin in a magnetic field and with $h \equiv g\mu_B B$ write

$$\mathcal{Z}_S = \sum_{m_1 = -S}^S e^{\beta h m_1} \sum_{m_2 = -S}^S e^{\beta (h + J m_1) m_2} = \sum_{m = -S}^S e^{\beta h m} \frac{\sinh [(S + 1/2)\beta (h + J m)]}{\sinh [\beta (h + J m) / 2]}.$$

The remaining sum most probably cannot be calculated analytically.

For $S = 1/2$ the expression above simplifies to

$$\mathcal{Z}_{1/2} = \sum_{m = -1/2}^{1/2} e^{\beta h m} 2 \cosh \left[\frac{\beta (h + J m)}{2} \right]$$

that is,

$$\mathcal{Z}_{1/2} = 2 \left\{ e^{\beta h / 2} \cosh \left[\frac{\beta (h + J/2)}{2} \right] + e^{-\beta h / 2} \cosh \left[\frac{\beta (h - J/2)}{2} \right] \right\}.$$

This expression can be simplified to

$$\mathcal{Z}_{1/2} = 2 \left[e^{\beta J/4} \cosh (\beta h) + e^{-\beta J/4} \right]. \quad (31)$$

Finally, in zero field the result simplifies to

$$\mathcal{Z}_{1/2} = 4 \cosh (\beta J/4).$$

Let us calculate the internal energy and heat capacity in zero field. One obtains

$$U = -N \frac{\partial \ln \mathcal{Z}}{\partial \beta} = -\frac{NJ}{4} \tanh\left(\frac{\beta J}{4}\right),$$

where N is the number of two-spin systems. In the limit of low temperatures the hyperbolic tangent tends to 1 and one obtains the anticipated result $U = -NJ/4$ (the two coupled spins are parallel for $J > 0$). In the case of antiferromagnetic coupling, $J < 0$, one has $\tanh(\beta J/4) \rightarrow -1$ for $T \rightarrow 0$, so that for both ferro- and antiferromagnetic coupling one obtains $U = -N|J|/4$ at zero temperature.

The average spin value per two-spin system is given by

$$\langle S_z \rangle = \langle m_1 + m_2 \rangle = \frac{1}{Z} \frac{\partial \mathcal{Z}}{\partial (\beta h)}. \quad (32)$$

Using Eq. (31), one obtains

$$\langle S_z \rangle = \frac{e^{\beta J/4} \sinh(\beta h)}{e^{\beta J/4} \cosh(\beta h) + e^{-\beta J/4}} = \frac{\sinh(\beta h)}{\cosh(\beta h) + e^{-\beta J/2}}.$$

The susceptibility can be obtained by differentiating this expression with respect to the magnetic field. In particular, at zero field

$$\chi \propto \frac{1}{1 + e^{-\beta J/2}}.$$

In the ferromagnetic case $J > 0$ the exponential is very small at low temperatures, $\beta J \gg 1$, so that the susceptibility has a regular value, comparable with that of an isolated spin. To the contrary, in the antiferromagnetic case $J < 0$ the exponential is large and thus the susceptibility is very small. Try to explain this in physical terms and draw the dependence $\langle S_z \rangle$ on the magnetic field for the antiferromagnetic coupling at low temperatures.